

A General Method for the Synthesis of Perdeuterated Hydrocarbons.
The Syntheses of n-Octane-d₁₈ and 2,2,4-Trimethylpentane-d₁₈.

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Introduction

As part of a continuing study of the relationship of physical properties to hydrocarbon structure, the changes in the properties when deuterium is substituted for hydrogen in hydrocarbons have been under scrutiny in this laboratory. Earlier, benzene-d₆ and cyclohexane-d₁₂ were prepared¹ and the properties determined.^{2,3,4} The results were sufficiently interesting that the syntheses of a perdeuterated normal paraffin and a perdeuterated branched-chain paraffin hydrocarbon were undertaken.

Although the literature^{5,6,7,8} records the preparation of a number of perdeuterated hydrocarbons, none of the procedures appeared to be satisfactory for the synthesis of molar quantities of perdeuterated aliphatic hydrocarbons in the C₆ to C₁₂ molecular weight range. The reported syntheses may be divided into two broad classes:

- (1) syntheses starting from available chemical intermediates and utilizing classical chemical reactions to construct the desired perdeuterated molecule. An example of this procedure is the synthesis of spiro-pentane-d₈ starting from calcium carbide by House, Lord and Rao.⁹
- (2) syntheses starting from a hydrocarbon possessing the same carbon skeleton as that desired in the final product and involving exchange of the hydrogens of the hydrocarbon with the deuterium atoms in a deuterium-containing molecule, e.g., D₂O, D₂SO₄. The synthesis of benzene-d₆ by Ingold and coworkers¹⁰ is a classical example of this approach.

Group (1) syntheses suffer from the fundamental disadvantage that each hydrocarbon structural-type requires a different synthetic route. Further, as the carbon skeleton of the molecule becomes more complex, the number of synthetic steps frequently increases rapidly. Since group (2) routes do not have these disadvantages, the present effort was confined to developing a procedure of this type but avoiding the problems noted below.

The exchange of deuterium between deuteriosulfuric acid and aromatic hydrocarbons proceeds readily at temperatures where no skeletal changes or other side reactions occur to any significant extent. Unfortunately, with aliphatic hydrocarbons, Setkina and coworkers¹¹ have found that under mild conditions only the tertiary hydrogens are exchanged. Under forcing conditions the expected carbonium ion rearrangements accompany the exchange.¹² Similarly, Dixon and Schiessler¹³

found that the vapor phase exchange between deuterium oxide and hydrocarbons is attended by significant cracking and/or isomerization.

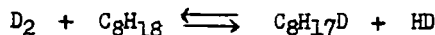
In contrast, Burwell and coworkers^{14,15,16,17} in their classical study of the mechanism of hydrogen exchange observed that the exchange of deuterium gas with aliphatic hydrocarbons proceeded rapidly in the vapor phase over metal catalysts and was accompanied by little or no carbon skeletal rearrangements. This procedure suffers only from the disadvantage that for the synthesis of molar quantities of a C₆ to C₁₂ paraffin hydrocarbon extremely large volumes (of the order of thousands of liters at STP) of deuterium must be used. Since our laboratory, like many others, lacks the facilities for the safe handling and compression of large amounts of hydrogen, a scheme involving the direct deuterium-hydrocarbon exchange but avoiding the handling of large amounts of deuterium was developed.

The Apparatus

Figure 1 is a flow diagram of the apparatus. A complete description of the apparatus and full experimental details may be found in reference 18.

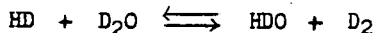
The principal operations occurring in the system are:

- (1) Hydrogen-deuterium gas is continuously circulated through the entire apparatus.
- (2) In the "deuterator" section this gas mixed with hydrocarbon vapor passes over a pelleted nickel on kieselguhr¹⁹ catalyst. A statistical distribution of deuterium and hydrogen atoms between the gas and the hydrocarbon results, e.g.,



The partially deuterated hydrocarbon is then separated by condensation and the hydrogen-deuterium gas passes to the "regenerator" section.

- (3) Here, the hydrogen-deuterium gas mixed with superheated deuterium oxide vapor is passed over the nickel on kieselguhr catalyst. The gas is re-enriched in deuterium from the heavy water



and as the gases leave the "regenerator" the water is separated by condensation while the hydrogen-deuterium gas returns to the "deuterator" section. The hydrogen-water equilibrium constant can be expressed as:²⁰

$$\log K = \frac{928}{4.57 T} - 0.1320$$

where

$$K = \frac{[\text{D}_2\text{O}][\text{H}_2]}{[\text{H}_2\text{O}][\text{D}_2]}$$

K is 1.980 at 200° and decreases as the temperature increases. Therefore, the regenerator was maintained at 300° C.

By this technique, the advantages of both the deuterium-hydrocarbon and deuterium oxide-hydrocarbon exchange processes are realized without the disadvantages of either. Although the hydrocarbon was in contact with approximately 1000 liters of deuterium gas during each twenty-four hour period of operation, there were only 12 liters of gas in the apparatus at any given time.

The apparatus was all glass except for the circulation pump which consisted of two counteracting sylvon bellows. Neither the deuterium oxide nor the hydrocarbon came in contact with the pump.

Since the maximum transfer of deuterium from heavy water to hydrocarbon is obtained by passing the hydrocarbon through the deuterator only once per charge of heavy water to the boiler, the following procedure was used. Hydrocarbon was fed slowly from reservoir A, Figure 1, into the incoming deuterium stream. At the entrance to the catalyst chamber the hydrocarbon was vaporized and the mixture of gases passed over the catalyst. On leaving the catalyst the hydrocarbon was separated from the hydrogen by condensation and stored in reservoir C. In contrast, the heavy water was continuously vaporized in the boiler, J, passed over the catalyst in the regenerator, condensed, returned to the boiler, revaporized and so on. When all of the hydrocarbon charge had passed from reservoir A to reservoir C, it was returned to A and a fresh charge of heavy water placed in the boiler, J.

With this procedure the variables which determine the amount of deuterium transferred from the water to the hydrocarbon per charge of heavy water are:

- (1) rate of throughput of the hydrocarbon
- (2) deuterium content of the entering hydrocarbon
- (3) moles of hydrocarbon passed per cycle
- (4) rate of hydrogen-deuterium gas flow
- (5) rate of heavy water flow through the regenerator
- (6) moles of water in the boiler
- (7) deuterium content of the water.

Since the temperature and the rates of throughput of hydrocarbon, hydrogen-deuterium gas and water vapor can be so adjusted that the H-D exchange equilibria are continuously maintained in the deuterator and regenerator catalyst chambers, it is possible to express the rate of decrease of the deuterium concentration of the water with time as a function of the variables listed above.¹⁸ The differential equation was integrated to yield:

$$t = \frac{1}{K} \ln \left(\frac{[\text{HC}] - [\text{D}_2\text{O}_{\text{start}}]}{[\text{HC}] - [\text{D}_2\text{O}_{\text{end}}]} \right)$$

where

t = time for passage of the complete hydrocarbon charge through the deuterator (time of one "cycle")

K = a constant

$[\text{HC}]$ = concentration of deuterium in the hydrocarbon (expressed as the fraction of the H + D atoms that were D) at the beginning of the cycle

$[\text{D}_2\text{O}_{\text{start}}]$ = concentration of deuterium in the water at the start (expressed as the fraction of the H + D atoms that were D)

$[\text{D}_2\text{O}_{\text{end}}]$ = concentration of deuterium atoms in the water at the completion of the cycle (expressed as the fraction of the H + D atoms that were D).

The last quantity is the only unknown and once it is calculated from the equation the number of deuterium atoms transferred from the water to the hydrocarbon can be obtained easily. Thus, the number of equilibrations (or cycles) to obtain any given amount of a hydrocarbon of a given deuterium content may be predicted.

n-Octane-d₁₈

Using the nickel on kieselguhr catalyst and a deuterator temperature of 115-130°, approximately 100 g. of n-octane-d₁₈ were synthesized from Phillips Research Grade n-octane. The hydrocarbon was cycled over the catalyst nine times, a fresh charge of heavy water being used for each cycle. The final deuterocarbon was fractionally distilled (14 fractions) and the fractions analyzed by vapor phase chromatography. As shown in Table I, the first fraction contained essentially all the products of cracking and isomerization. This was expected since any product which resulted from cracking or isomerization of n-octane would be lower boiling.

Table I

Impurity Concentrations in n-Octane-d₁₈

Fraction	Concentration of Impurity in the Fraction (% by weight)	Concentration in the "Crude" Product (% by weight)
1	10	0.2
2	0.2	0.01
3-13	not detectable <0.02	<0.001
Total		~0.2

The isotopic concentrations in fractions 3-13, as obtained by density determination, were 99.1% D, 0.9% H.

2,2,4-Trimethylpentane-d₁₈

An attempt was made to synthesize 2,2,4-trimethylpentane-d₁₈ by the procedure used for the synthesis of n-octane-d₁₈. With the same rate of hydrocarbon feed to the catalyst, the product from the first cycle had approximately 30% of the expected deuterium content. Two more cycles through the apparatus did not appreciably increase the deuterium content of the hydrocarbon.

The lack of equilibration was due probably to the phenomenon described by Burwell,^{14,15} i.e., that complete equilibration between deuterium and a hydrocarbon molecule on a catalyst surface will not take place past a quaternary carbon atom. The quaternary carbon atom in 2,2,4-trimethylpentane has attached to it a 2-methylpropyl group and three methyl groups. Should the 2-methylpropyl group be chemisorbed on the catalyst surface one-half of the hydrogen atoms in the hydrocarbon molecule will equilibrate with deuterium and the deuterium content will be half that produced by an equivalent chemisorption of n-octane and deuterium. However, chemisorption of the hydrocarbon molecule via a methyl group (the probability of this event is 0.5, on the basis of the hydrogen atoms accessible to the catalyst) will yield a deuterium content one-eighteenth that produced by the equivalent chemisorption of n-octane and deuterium.

An attempt was made to produce equilibration by raising the temperature of the catalyst chamber. Not only would complete equilibration be favored by more frequent adsorption-desorption of the hydrocarbon on the catalyst surface, but the temperature increase would also increase the probability of a methylene type adsorption

suggested by both Burwell⁵ and Kemball.²¹ Such adsorption would by its nature increase the deuterium content of the molecule.

Equilibrium between deuterium and the hydrocarbon was approached rapidly in the 181-195° range but was accompanied by extensive cracking and isomerization. A temperature of 154-164° was used as a compromise between a rapid reaction with extensive production of impurities and a very slow reaction without.

The apparent "equilibrium constant" of the reaction between deuterium gas and 2,2,4-trimethylpentane in the deuterator at this temperature was 0.3, whereas the equivalent value for n-octane was 2. These values were obtained by analysis of the products from the deuterator and depended, in the case of 2,2,4-trimethylpentane, on the residence time on the catalyst.

Table II

Impurity Concentrations in 2,2,4-Trimethylpentane-d₁₈

Fraction	Concentration of Impurity in the Fraction (% by weight)		Concentration in the "Crude" Product (% by weight)
	Cracking	Isomerization	
1	55	< 0.02	1.2
2	10	< 0.02	0.28
3	1.6	< 0.02	0.074
4	0.1	< 0.02	0.0082
5-9	< 0.02	< 0.02	< 0.02
10	< 0.02	0.2	0.017
11	< 0.02	3.2	0.024
residue	< 0.02	5.3	0.11
Total			~1.8

Three isomer impurity peaks were obtained in the vapor phase chromatogram. As the retention times of two of the pairs of octane isomers are almost identical, these three peaks could be due to five isomers. The total concentration of all isomers in the original deuterated product is believed to be less than 0.2% as based on chromatographic results on the fractionated material. The major impurity is probably a deuterated 2,4-dimethylhexane or 2,5-dimethylhexane. Two other isomers, formed in concentrations approximately one-tenth those of the major impurity, were 2,2-dimethylhexane and either 3,3-dimethylhexane and/or 2,2,3-trimethylpentane.

Distillation fractions 5-9 had no isomerization and cracking impurities detectable by vapor phase chromatography and were taken as high-purity deuterated 2,2,4-trimethylpentane. The vapor phase chromatography results indicate that the carbon skeleton of this material is more than 99.9% 2,2,4-trimethylpentane. As determined by density measurements, the isotopic purity of the final product is 97.4% D.

In conclusion, it should be emphasized that the problem of extremely slow equilibration observed with 2,2,4-trimethylpentane is probably confined to molecules possessing quarternary carbon atoms. It is expected that all other types of aliphatic hydrocarbons will behave in a fashion very similar to that of n-octane.

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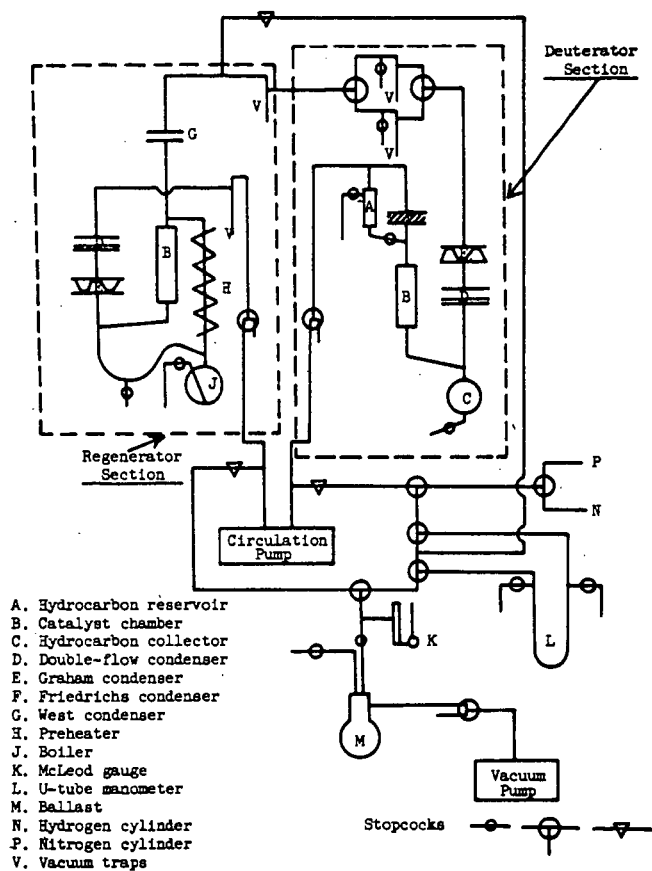


Figure 1. Schematic Diagram of Deuteration Apparatus